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Production process of carboxymethyl cellulose

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ABSTRACT

Production process of carboxymethyl cellulose
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Carboxymethyl cellulose (CMC) is a widely used synthetic, powder-like chemical compound. It is used as an additive for its wide variety of attributes, perhaps most commonly for its ability to raise viscosity in a solution. CMC can be synthesized from many different cellulose sources, making it a rich and active field of study.

The objective of this bachelor's thesis was to build a process description of CMC production: identifying major factors causing variation within the production process, investigating major quality attributes and their control in the production, and examining the chemical phenomena involved within the materials and the synthesis of CMC. This bachelor's thesis was based on literature reviews, published experimental studies, and information provided by various CMC manufacturers. The CMC production line from Nouryon in Äänekoski was used as an example of industrial level CMC production.

The main factors causing variation in the production of CMC were found to be different cellulose sources and different target quality grades of CMC. It was concluded on the basis of this variation, that universal process conditions for CMC production do not exist. The most significant quality attributes were found to be solution viscosity, purity, and degree of substitution. The quality attributes were found to be affected by many different factors in different production steps. The etherification step was found to be a central production step affecting the quality attributes.

Keywords: cellulose ether, carboxymethyl cellulose, mercerization, process description, process control

TIIVISTELMÄ

Karboksyylimetyyliselluloosan valmistusprosessi
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Karboksyylimetyyliselluloosa (CMC) on laajalti käytetty synteettinen jauhemainen kemiallinen yhdiste. Sitä käytetään lisäaineena lukuisten ominaisuuksiensa vuoksi, joista yleisin lienee sen kyky nostaa liuoksen viskositeettia. CMC:tä voidaan syntetisoida lukuisista erilaisista selluloosalähteistä, mikä tekee siitä yleisen ja aktiivisen tutkimusalueen.

Tämän kandidaatintutkielman tavoite oli muodostaa CMC:n valmistuksen prosessikuvaus: tunnistaa tärkeimmät tuotannollista vaihtelua aiheuttavat tekijät tuotantoprosessissa, tutkia keskeisiä laatuominaisuuksia ja selvittää, miten niitä hallitaan tuotannossa, sekä tutkia CMC:n materiaalien ja synteesin kemiallisia ilmiöitä. Tämä kandidaatintutkielma perustui kirjallisuuskatsauksiin, julkaistuihin kokeellisiin tutkimuksiin sekä useiden CMC-valmistajien tarjoamiin tietoihin. Nouryonin CMC-tuotantolinjaa Äänekoskella käytettiin esimerkkinä teollisen tason CMC-tuotannosta.

Tärkeimmät tuotannon vaihtelua aiheuttavat tekijät CMC:n valmistuksessa havaittiin olevan erilaiset selluloosalähteet sekä CMC:n laatuluokitukset. Niiden perusteella pääteltiin, että CMC:n tuotannossa ei ole yleisiä prosessiolosuhteita. Merkittävimmät laatuominaisuudet katsottiin olevan liuosviskositeetti, puhtaus ja substituutioaste. Lukuisilla tekijöillä monissa osaprosesseissa havaittiin olevan vaikutusta laatuominaisuuksiin. Eetteröintivaiheen havaittiin olevan keskeinen laatuominaisuuksiin vaikuttava osaprosessi.

Asiasanat: selluloosaeetteri, karboksimetyyliselluloosa, merserointi, prosessikuvaus, prosessin hallinta

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1 INTRODUCTION

The term *cellulose* is derived from a Latin term cella, meaning small room or a hut, coined by a French scientist Anselme Payen in 1830s. Payen was the first to separate wood into its components, naming the separated white fibrous material cellulose. Cellulose has been studied extensively since its discovery, bringing forth many new chemical derivatives and applications with cellulose as a raw material. Cellulose is an essential building block of the cell wall in plants; it is thus an abundant organic polymer in nature. As global environmental concerns are continually rising, cellulose and its derivatives are gaining growing attention as a possible part of the solution to a world in need of a shift away from nonrenewable materials. The chemical derivatives of cellulose can be categorized into cellulose esters and cellulose ethers. Carboxymethyl cellulose (CMC) is a significant cellulose ether.

Carboxymethyl cellulose is an odorless, tasteless, white to yellowish colored powder-like substance. CMC is an essential component in many manufacturing industries. CMC is water soluble and can maintain stability in pH of 3-10 (Turkki, 2018). It has many applications in different manufacturing industries because of its multifunctional properties: forming film, stabilizing, thickening, and controlling fluid loss in substances. Since CMC is harmless to consume in its pure form, it is also commonly used as an additive in food products. For example, it prevents precipitation in drinks, while also providing rich mouthfeel. It increases viscosity in syrups and pastes, but perhaps most famously it is used in ice cream industry, which benefits from all previously stated functions of CMC, while also raising melting resistance and reducing the formation of ice crystals. These examples might give some idea of the versatility of CMC. CMC is listed under the E number E466 or E469.

Around 192 million tons of cellulose is produced globally in a year, with around 97 % of cellulose fibers being used in paper manufacturing as a structural material. CMC has the widest commercial volume of all cellulose ethers, but precise information on cellulose derivative markets is not widely available. The information is marketed with a high price – mainly to companies – and the information in the reports is confidential. Therefore, estimates derived from different models vary. One study estimated global CMC

production in 2016 to be 46 000 tons, or $209 million, excluding Chinese markets. (Turkki, 2018)

Some of the significant producers in the CMC market globally are Akzo Nobel NV, Sidley Chemicals Co., Ltd, Anqiu Eagle Cellulose Co. Ltd, Ashland Global Holdings Inc., CP Kelco, Daicel Corporation and lately Nouryon, with the acquisition of product line from J.M. Huber Corporation. In Finland, CMC is manufactured in Äänekoski by Nouryon.

The goal of this bachelor's thesis was to build a process description of CMC production throughout its production process and identify the major factors causing variation within the production process. As the scientific work in CMC production focuses mostly on developing chemistry to synthesize CMC from different cellulose sources at laboratory scale, literature on industrial scale production of CMC is limited. Therefore, the process description in this work is presented using mainly the production lines from Nouryon, (formerly CP Kelco) in Äänekoski as an example. Other examples are from experimental laboratory studies, where CMC is produced from different materials. In addition, there is no single way to produce CMC, as there exists a lot of factors to be considered, for example from varying raw materials to different target qualities, which may change the conditions of the production.

The work is divided into three main sections. Section 2 examines the product quality attributes of CMC, explores potential new raw materials and chemistry behind the production process. In Section 3, process steps, or the typical series of activities in the industrial production of CMC are examined. Section 4, process control, strives to explain the quality variation and optimum operation range from the perspective of process conditions and controllable variables. Finally, Section 5 summarizes the work briefly.

2 CMC PRODUCTION

In this section, CMC production is investigated widely through its basic production requirements, raw materials, and different chemical forces and phenomena behind materials and reactions.

2.1 Product quality attributes

The list of typical quality attributes of CMC is long, and even contains some very basic attributes, such as color, size, smell, taste, weight, and even packaging (Tiihonen, 2017). In addition, features of CMC alone can be defined by many different attributes, including the degree and evenness of substitution, the degree of polymerization, particle size distribution, impurities, and pH. Therefore, the investigation will be limited to some of the most significant controlled product quality attributes: solution viscosity, purity, and degree of substitution.

2.1.1 Solution viscosity

Viscosity refers to the thickness of a fluid, or its ability to resist deformation. CMC itself cannot be described as a particularly viscous substance, as it is a powder-like substance by nature. However, CMC is exploited commercially mainly because of its ability to raise viscosity in the target solution. This attribute is called solution viscosity. The solution viscosity in the production process of CMC is adjusted with hydrogen peroxide (H_2O_2) before granulation (Tiihonen, 2017). Further inspection for other factors concerning solution viscosity is done in Section 4.2.1. Manufacturer Sidley Chemical divides solution viscosity into three categories: high, medium, and low, defined as 1 % of the solution consisting of CMC. High viscosity CMC has around 5000-8500 Pa·s for 1 % solution, medium ranging between 1000 to 5000 Pa·s, and low being around 5-1000 Pa·s (Sidley Chemical co., 2021).

2.1.2 Purity

The color of CMC is determined by its purity, with white being the purest. CMC may contain many different impurities, such as micro-organisms and heavy metals, but generally, the main impurities of CMC are solvent residue and salts produced as a side-

product (Stigsson et al., 2004). Washing is used in the manufacturing process to reach a refined grade. The washing process uses water and solvents to separate CMC of the salts. The salts in question are sodium chloride and sodium glycolate (Ambjörnsson, Schenzel, & Germgård, 2013) – and they are a by-product of etherification.

CMC can be divided into different grades according to the quality of the product. Some manufacturers even categorize it by its intended use (e.g., mosquito repellent grade), as CMC has many controllable attributes besides purity. Mondal et al. (2015) defined four different grades for CMC according to purity: technical, semi-purified, purified, and extra purified. The grades were defined according to the percentual content of both CMC and salts. For technical grade, content of <75 % CMC and >25 % salt is approvable. Technical grade CMC is often used in detergents and in mining industry as depressants in mining flotation. Semi-purified grade consists of around 75-85 % CMC and 15-25 % salt. It is often used in oil and gas drilling, reducing fluid loss by forming a filtration cake on drill hole wall. Purified grade is defined as having >98 % CMC content and <2 % salts and is popular for example in paper industry; when added to pulp, it improves paper quality and pulp processability. Finally, extra purified grade is required in pharmaceutical and food industries. Its requirement is >99.5 % CMC content and only <0.5 % salts. This grade is also called cellulose gum.

2.1.3 Degree of Substitution

The degree of substitution (DS) is a chemical term, describing the substitution of a hydrogen in a hydroxyl group by carboxymethyl within a single glucose unit. Determining DS is important because it is the primary attribute defining CMC properties. By determining the degree of substitution, the physical and chemical properties of CMC, such as solubility, emulsibility, acid resistance and salt tolerance, can be controlled and adjusted (Sidley Chemical co., 2013a). The degree of substitution is a wide topic and is therefore more closely investigated in the Sections 2.3.4 and 4.2.3 through chemistry and process control.

2.2 Raw materials

Investigating new sources of cellulose, solvents and solvent mixtures is a rich and active field of research. Ideally, the goal is to find an environmentally friendly and cheap way

to dissolve an abundantly found and sustainable cellulose source, from which new products can then be processed.

2.2.1 Cellulose sources

CMC can be produced from many different sources containing cellulose. Therefore, the process may also vary according to different manufacturers, raw materials, and dissolving agents used.

Cellulose is the backbone structure of the CMC molecule, and the main raw material in the CMC production process. Wood and cotton linters are commonly used as sources of cellulose. While cotton linters contain significantly more cellulose than wood relative to weight, cotton linter supply is often limited compared to wood. The CMC manufacturing plant in Äänekoski, Finland, uses dried cellulose from pine and birch trees (Tiihonen, 2017). To answer the growing need for sustainable new sources of cellulose, alternatives to conventional sources like wood and cotton linters are being searched and investigated all over the world. Nonconventional cellulose sources have then been drawing attention, especially sources that are abundant in different geological locations. For example, Saputra, Qadhayna, & Pitaloka, (2014) did an experimental study, where their goal was to investigate whether CMC can be synthesized from water hyacinth cellulose. They presented water hyacinth from South America as a highly problematic, fast-growing, and widespread wild weed - yet rich in cellulose. They experimented with varying sodium hydroxide (NaOH) concentrations and ratios of isobutanol and ethanol as a solvent for isolating cellulose from water hyacinth. The isolated cellulose was further processed into CMC. It was concluded that water hyacinth is a viable source of cellulose for CMC, with the highest DS value obtained from a solvent mixture of 80 % isobutanol and 20 % ethanol. However, they suggested that an alternative solvent to isobutanol should be explored, since isobutanol by its chemical properties may hinder alkalization of CMC.

Recyclable materials are another potential and more environmentally sustainable source of cellulose. (Ünlü, 2013) examined recycled newspaper as a source of cellulose for CMC production. The newspaper had first to be purified with alkaline peroxide to remove ink and solubilized impurities to produce recycled cellulose. The cellulose was then dissolved in a solution with NaOH and hydrogen peroxide, after which the pulp was synthesized into CMC and washed with ethanol. The result was a moderate amount of CMC, which

had a DS range of 0.3 to 0.6. The research concluded that the obtained CMC could be used in non-food applications as an additive and thickener.

2.2.2 Solvents and other raw materials

The main emphasis within a study of a new cellulose source is heavily on the dissolution of cellulose, since dissolution is a complicated step due to the poor solubility of cellulose, and because of the varying chemical compositions and properties between different cellulose sources. As a result, the list of developed solvents and solvent mixtures is vast, and the research field is active. One common mixture of solvents is ethanol (EtOH) and isopropanol (IPA), which were used by Saputra et al. (2014), but also in industrial CMC production at CP Kelco Äänekoski manufacturing plant (Tiihonen, 2017). More solvents and different solvent categories are introduced in Section 2.3.

According to Tiihonen (2017), other essential chemicals include NaOH, monochloroacetic acid (MCA), H_2O_2, and hydrochloric acid (HCl). NaOH is commonly used in CMC production together with an alcohol, such as ethanol, as a solvent. NaOH is also used as a reactant both in alkalization and etherification reactions, as is shown in Section 2.3. MCA is used in the etherification step to add carboxymethyl groups into alkali cellulose, forming CMC molecules. HCl is a key component in the neutralizing process, where it neutralizes excess NaOH, adjusting pH of the product.

2.3 Chemistry

Understanding the chemical phenomena behind CMC production process is of utmost importance, especially when implementing a CMC production process using an unorthodox cellulose source. Although the synthesis steps of CMC have been widely established, to optimize yield and the DS of the CMC, different cellulose sources require different synthesis conditions, and possibly different pretreatment methods as well.

Central subjects inspected in this subsection are cellulose at a molecular level, the dissolution of cellulose, CMC synthesis steps and products, and the degree of substitution.

2.3.1 Cellulose

Cellulose is an abundant renewable biopolymer; a long-chained organic compound found from plants. Its chemical formula is $(C_6H_{10}O_5)_n$. Cellulose is composed of linear D-anhydroglucopyranose units (AGU), which are linked together by β-(1-4)glycosidic bonds. Degree of polymerization (DP) is used to define the size of the cellulose molecule. Its value reflects the amount of AGU in the molecule. These long molecule chains can also form various kinds of hard and stable crystalline parts, caused by intra- and intermolecular hydrogen bonds. The molecular structure of cellulose also causes variable polarity in different parts of the molecule. The molecule has hydrophilic characteristics caused by hydroxyl groups in the equatorial direction of the glucopyranose ring. Yet due to the hydrogen atoms of the C-H bonds, the axial direction of glucopyranose ring is hydrophobic. Crystallization and polarity may cause the dissolution of cellulose to be quite challenging. (Medronho & Lindman, 2014)

2.3.2 The Reaction stages: Mercerization and Solvents

From a chemical point of view, the reaction stages of CMC manufacturing process can be summarized into two steps: mercerization and etherification. The purpose of mercerization is the formation of alkali cellulose, while the etherification step produces CMC. Mercerization begins – like with all cellulose ethers - with the dissolution of cellulose.

Mercerization is a step where solvents are used to swell and dissolve the cellulose pulp, increasing the reactive surface and facilitating the penetration of NaOH. Cuissinat & Navard (2006) defined five different ‘modes’, that are useful in describing the behavior of cellulose fibers dipped in chemicals and numbered in order from the best quality solvent to worst. Mode 1 is used in describing a solvent or a solvent mixture that is the most effective. In mode 1, cellulose is quickly dissolved into rod-like fragments, bypassing the swelling stage altogether. Mode 2 includes the swelling stage, transforming the cellulose in what could be described as a large ‘ballooning’ motion, reaching a point of bursting, and finally dissolving. Mode 3 is the same as mode 2, except that cellulose does not go through the dissolution phase but is instead left in a swollen state, experiencing only a partial dissolution inside the balloon. In mode 4, the cellulose goes

through weak, homogenous swelling and no dissolution. Finally, mode 5 is the worst solvent quality, where the chemicals do not interact with the cellulose in any way.

The problem with dissolving cellulose is that it does not respond well to usual solvents like water and organic solvents; cellulose is too resilient. That is why a proper solvent combination is critical to a successful dissolution. The objective of the dissolution process is to break down the hydrogen bond network of cellulose with a solvent in a water-alcohol slurry, typically at room temperature, 20 to 30 ºC. Medronho & Lindman (2014) referenced in their article a four-way categorization of cellulose solvents: cellulose dissolution is characterized as an acid-base process, where the first two categories are determined by cellulose acting either as an acid or a base, depending on the solvent method used. The other two categories are non-derivatizing and derivatizing solvents. A vast list of possible solvents and solvent combinations have been found - still many of them without commercial success. Aqueous NaOH - being cheap, available, and easy to handle - is possibly the most common commercial solvent. Other non-derivatizing aqueous base-solvents listed in Medronho & Lindman (2014) include LiOH, quaternary ammonium hydroxides, $LiClO_4 \cdot 3H_2O$ and water-salt systems like $LiSCN/H_2O$ and $ZnCl_2/H_2O$. Derivatizing solvents include the first ever recorded dissolver combination of HNO_3/H_2SO_4. More recent and an important derivatizing solvent is a combination of alkali and carbon disulphide (CS_2), despite raised environmental issues. (Medronho & Lindman, 2014)

The chemical reaction for mercerization is depicted in Equation 1 (Isotalo, 2004). The swollen and dissolved cellulose is turned into alkali cellulose (or Na-cellulose) in an alkalization reaction, when NaOH reacts with the exposed hydroxyl groups

$$C_6H_{10}O_5C_6H_9O_4 \cdot OH + NaOH \rightarrow C_6H_{10}O_5 \cdot C_6H_9O_4 \cdot ONa + H_2O \quad (1)$$

2.3.3 The Reaction stages: Etherification

In the etherification stage, alkali cellulose from the mercerization stage reacts with added MCA in the presence of NaOH at around 50–70 ºC (Ambjörnsson et al., 2013). On a molecular level, a hydroxyl group replaces a hydrogen with a carboxymethyl group (see Equation 2). This reaction is also called carboxymethylation. NaOH also contributes to

unwanted by-products when reacting with MCA: reaction salts sodium glycolate and sodium chloride, which are considered impurities. Therefore, the product of this reaction is technical grade CMC, which gets refined later in the process, if necessary.

The carboxymethylation reaction for the etherification process is summarized in Equation 2 (Isotalo, 2004), where in order of appearance alkali-cellulose reacts with MCA and NaOH to form CMC and HCl.

$$C_6H_9O_4 \cdot ONa + ClCH_2COOH + NaOH \rightarrow C_6H_9O_4 \cdot O \cdot CH_2OONa + HCl \quad (2)$$

The reaction equation for the by-products is depicted in Equation 3 (Stigsson et al., 2004). MCA reacts with NaOH to form the salts sodium glycolate and sodium chloride.

$$ClCH_2COOH + 2NaOH \rightarrow HOCH_2COONa + NaCl + H_2O \quad (3)$$

2.3.4 Degree of Substitution

The added carboxymethyl groups define the properties of CMC, thus etherification is the part where the functional properties of CMC are formed. The number of added carboxyl groups is described as the degree of substitution as explained in section 2.1.3. DS is a significant value for defining the functional properties of CMC, as it is directly proportional to the CMC's solubility for water and rheological properties. The properties for water solubility begin at ≥0.6 DS. DS of ≤0.2 indicates fibrous character. For commercial CMC, the DS value is generally around 0.4–1.5. The theoretical maximum value of DS is 3, as one anhydroglucose unit has three substitutable hydrogen atoms on hydroxyl groups in C_2, C_3 and C_6. By repeating the reaction steps, it is possible to approach near the theoretical maximum DS. (Ambjörnsson et al., 2013)

According to Ambjörnsson et al. (2013), the uneven distribution of substitution also poses problems for a functioning CMC molecule. Segments inside the molecule with a low DS can form gel-like, visible swollen particles in the water solution, instead of dissolving into water. This is a problem that can be mitigated by raising the total degree of substitution.

2.3.5 Neutralization

After the main reaction stages the excess NaOH is neutralized by adding HCl into the slurry, reaching neutral pH levels. While CMC remains stable in a wide range of pH, it is the most stable in the pH range 6.5–9.0 (Sidley Chemical co., 2013b). Mixing NaOH with HCl in a water solution is a classic example of neutralization chemistry, where the chemical products are NaCl and H_2O. The reaction is finally terminated by the neutralization step.

3 PROCESS STEPS

Industrial production comprises production at the largest scale. A single production line at the CMC production plant in Äänekoski produced over 14 000 tons of CMC annually in 2017 (Tiihonen, 2017). In this section, the goal is to describe the typical industrial process steps and material flow for producing CMC, from raw materials to packaging. Since literature on industrial scale production of CMC is limited, the process steps are described using mainly the CMC production lines at Nouryon in Äänekoski as an example.

3.1 Process description

Manufacturing of CMC is a multistage process. The production process according to the manufacturer CP Kelco Ltd at Äänekoski in 2017 – since then bought by Nouryon – can be summarized into 11 subprocesses: pulp milling, mercerization, etherification, neutralization, washing, solvent recovery, granulation, drying, screening, grinding, and packing (Tiihonen, 2017). The process is summarized in a process graph in Figure 1.

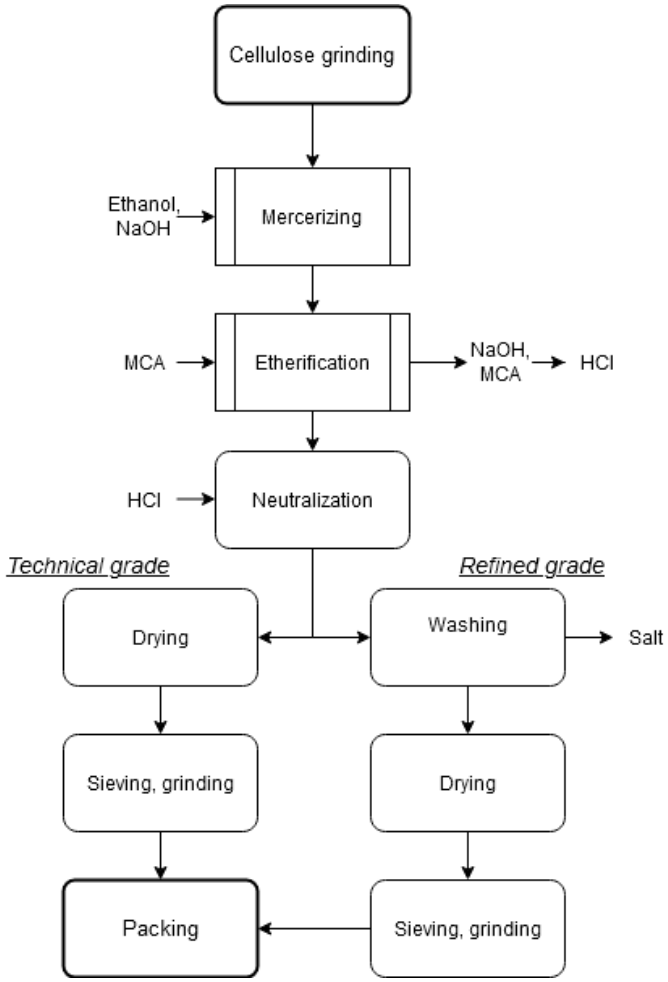

Figure 1. CMC process graph.

The CMC production starts from cellulose grinding. In modern CMC production, separate reactors for the reaction stages have widely been replaced by a one-step slurry process (Ambjörnsson et al., 2013). The slurry process is a batch process - consisting of mercerization, etherification, and neutralization.

After neutralization, the newly created technical grade CMC is directed into a buffer tank dampening flow fluctuation. From this point on the process becomes continuous by type. The production flow is divided between refined and technical grades. The high purity CMC is produced from the refined grade flow, which differs from the technical grade flow by including the washing process, that extract salts from CMC. Aside from the washing process, the different production lines are identical; a stripper separates and recycles the solvents from the CMC, the CMC is dried, granulated, and packed. (Tiihonen, 2017)

3.2 Cellulose grinding

The process starts with stacked cellulose bales being separated into sheets and transported into milling through metal detectors. In the Nouryon processing plant, the milling process involves two stages: shredding and grinding. The shredder processes cellulose sheets into a few square centimeter sized pieces. The pieces are then transported pneumatically into silos for containing. Screw conveyers transfer cellulose pieces from the silos into grinders, which further reduce their particle size distribution into a powder-like substance. (Tiihonen, 2017)

3.3 Mercerization

The slurry process starts with mercerization, which is the first reaction step. Mercerization improves the accessibility of hydroxyl groups in the cellulose molecule, and transforms the cellulose unit into alkali cellulose, which is reactive towards MCA.

The cellulose is inserted into the reactor together with solvents, NaOH and alcohol (usually ethanol or isopropanol) at around 20–30 ºC (Ambjörnsson et al., 2013). The components are mixed into a homogenous substance, in which the alcohol and NaOH solution acts as a reaction medium, swelling the cellulose fiber, reducing the number of intermolecular hydrogen bonds, thus increasing the reactive surface for NaOH to react.

3.4 Etherification

The CMC molecule is created in the etherification stage. The etherification reaction is triggered in the reactor by adding MCA into the mixture. The MCA reacts strongly with alkali cellulose when the reactor temperature is raised to 50–70 ºC (Ambjörnsson et al., 2013). Some of the hydroxyl groups get substituted with carboxymethyl groups, and so carboxymethyl cellulose is formed. The temperature of the reactor is lowered, bringing the etherification to a stop. The reaction also produces NaOH and MCA as by-products.

3.5 Neutralization

After the main reaction stages, the surplus of NaOH must be removed from the product. It is achieved through neutralization. Hydrochloric acid (HCl) is added into the water-alcohol mixture, neutralizing excess NaOH and adjusting the pH of the mixture into neutral levels. Neutralization finally terminates the reaction process, and the product is pumped into an expansion tank. (Tiihonen, 2017)

3.6 Washing

Washing is a process where unwanted by-products – mainly salts – are separated from the CMC. The salt is separated from the CMC using a water-alcohol mixture. Usually the alcohol is aqueous methanol, ethanol, or propanol (Nader et al, 1985). Salt dissolves into water, while the solvent prevents CMC from being dissolved as well.

The washing process includes two stages; first, the CMC slurry is pumped into a washing tank together with water and solvent. The salt dissolves into the water inside the tank, where the contents are then mixed, and the temperature is lowered to around 25–40 ºC. Second, the contents are transferred into a 5-staged flat filter, through which the salt drains off together with the solvent by a vacuum. The solvent flows countering the current of CMC salts. Rest of the solvent is removed by running steam through a stripper pipe and processed for reuse. (Tiihonen, 2017)

3.7 Granulation

At this point of the process, the viscosity of the product is adjusted by adding H_2O_2 to CMC, bleaching the product at the same time (Tiihonen, 2017). The particle size distribution of CMC is defined in the granulation process. Granulation is a process, where materials are shaped into grains or granules. Granulation can be used to determine CMC properties, such as flowability and compressibility. Particle size distribution of produced CMC may vary between different manufacturers.

The granulation process is carried out inside a stirring unit. At this point, CMC is typically moist with leftover alcohol-solvent and purified water. Water is used as a binder to the

granules, while heat and steam are used to evaporate and remove the rest of the solvents consisting of alcohol by running steam countercurrent to the CMC material inside the stirring unit. The product moves horizontally through the rotating unit. The preferable density of CMC granules is 450–650 g/l, and water content around 30 to 42 %, while the preferable residence time in granulation may vary from 1 minute up to even 30 minutes (Nader et al., 1985). The main methods to control the granulation quality are controlling the feed of the steam, the residence time, and stirring speed.

3.8 Drying

After granulation, the product is given time to let leftover H_2O_2 degrade. H_2O_2 is not a flammable substance, but it is an oxidizer, and therefore leftover traces may create a fire hazard, and even an explosion hazard in the drying process. (Tiihonen, 2017)

According to Tiihonen (2017), the final humidity of the CMC product is around 8–10 %, varying according to the required CMC attributes, such as solubility, bulk density and overall processability; screening and grinding. In addition, loose CMC dust is collected by filters and added back to the final product. In the drying process, mainly temperature and running time are controlled to reach the wanted humidity. The particle size distribution can also affect drying time, as bigger particles reduce total evaporation area. This means that differences in granulation should probably be taken into account in the drying process.

3.9 Sieving, grinding, packing

Finally, CMC product goes through a screening process, reaching a more uniform final product. The screening includes three overlapping flat screens, which sift the larger particle sizes to a grinder. The product that passes through the screening process is directed into a silo. Dust is directed into a silo specifically for dust. Eventually, the product is transferred into mixing silos and product silos, from where the product is packed into bags. (Tiihonen, 2017)

4 PROCESS CONTROL

This section investigates CMC production process control according to production variance. Production variance can be defined as difference or uncertainties of quality between produced units. Section 4.1 investigates the most significant factors causing quality variance to product quality. Section 4.2 investigates controllable variables; what product features can be controlled.

4.1 Process conditions

Process conditions are manipulated according to pre-defined recipes to achieve a wide variety of CMC grades. To reach a uniform quality, different process conditions must be met through adjusting variables. Typical causes for quality variations include temperature and pressure variations, catalyst addition, incomplete washing, poor mixing, drying and milling operations. In addition, upsets in product quality may also rise from unexpected factors, as well. These include factors, such as changes in raw materials and chemical compositions, and both machine and human failures and errors. High uncertainty in quality assessment can also compromise the product quality.

Stigsson et al. (2004) investigated quality variance in CMC production between different CMC grades. They hypothesized possible sources of variation rising mainly from raw cellulose variations and different processing steps, such as differences in reactor operations: catalyst addition, temperature and operation variation. They were also concerned with production variations in storage vessels, washing and drying processes. The product variations were mainly studied through viscosity and molecular weight distribution (MWD) measurements. In the next section, the process variation is investigated through raw materials and different process steps.

4.1.1 Raw material variations

Sections 2.2 and 2.3 explored the problems of different cellulose sources in cellulose derivative production. It is generally acknowledged, that cellulose resiliency and widely varying chemical compositions between different sources pose unique challenges to cellulose dissolving. The problems created by different cellulose sources have resulted in

a large list of developed solvents and solvent mixtures. It is possible, that different cellulose sources may cause variations in the final CMC product. It is thought that because high viscosity cellulose is difficult to dissolve, this could reflect on the molecular weight distribution of the product. Generally, materials requiring a larger amount of processing may be exposed to product quality variations. Changes in the MWD caused during the production can be investigated by comparing the MWD of the product to the MWD of the raw materials between different cellulose grades using, for example, size-exclusion chromatography. (Stigsson et al., 2004)

4.1.2 Reactor operations

CMC reactors can pose problems for investigating production variance, since the reactions are handled as a one-step slurry process. Further complicating the matter of inspection are reactants, often being harmful to health or otherwise hazardous. The results then can only be measured until the process has come to an end, with the product separated of extra chemicals. By the milling stage, samples can be taken and carefully compared against samples of different batches. (Stigsson et al., 2004)

As the CMC reaction stages are mainly driven by temperature adjustments – as introduced in Section 2.3 – deviation from the optimal temperature levels results in inferior quality products. Mercerization reaction requires temperatures around 20–30 ºC, while etherification reaction is initiated at around 50–70 ºC. It was noted by Stigsson et al. (2004) that a relatively high temperature (45 ºC) together with shorter contact time in mercerization results in an uneven distribution of substituents, which is due to the reaction area being reduced to the surface of the fiber. In the etherification step, deviation from the optimal temperature was found to decrease yield and increase salt production. However, the temperature variance of the etherification reaction was observed not to affect the evenness of the reaction.

4.1.3 Continuous production stages

Finally, it must also be hypothesized that the production stages after the reactor might induce quality variation. Rest of the significant process stages possibly affecting quality are the buffer tank, washing, drying, and grinding stages. The purpose of the buffer tank is to even out flow fluctuation after the reactor stage before the shift into a continuous

process. Here, an uneven dampening of flow may have possible effects on product quality variation. Both washing and drying, when done inefficiently or left incomplete, may leave unwanted salt or other side products into the final product, thus weakening the quality. In factory grinding, the grinding stage has been found to lower the viscosity of the product slightly (Stigsson et al., 2004). It is hypothesized, that the viscosity is lowered as a result from lowered degree of polymerization, which in turn results from physical cutting of fibers and raised temperature in the grinding stage.

4.2 Main controllable variables

Controllable variables can be considered as features – or attributes – which define the final product. The effects of the production on these variables may grow in proportion to the process steps needed and raw materials used. Section 2.1 introduced and determined the product quality attributes and their purpose in the product. In this section, the most important controllable variables are investigated through the production process steps. The section mainly describes, how different steps affect these variables and how they can be controlled. The most essential controllable variables were previously summarized into three: solution viscosity, purity, and degree of substitution.

4.2.1 Solution viscosity

Viscosity, or the ability of CMC to give deformation resistance to a target solution, is a key controllable variable, and perhaps the most common reason CMC is used in solutions. Several factors may influence CMC solution viscosity. To avoid confusion, these should be divided into factors in end use and in production processes. Concerning the end use of CMC, main factors affecting viscosity are solution concentration, pH value, temperature, and salts, (Sidley Chemical co., 2013b) many of them having an optimal range for viscosity performance. The emphasis of this section, however, is on the production process, which gives CMC the ability to raise the viscosity in target solutions.

Solution viscosity is directly proportional to the degree of polymerization – the length of the polymer chains. Other factors believed to be affecting solution viscosity are molecular weight distribution and evenness of substitution (Stigsson et al., 2004). Steps possibly affecting DP are the grinding stages, where rough physical processing together with increased temperature from friction may cut and shorten the polymer chains. However,

Stigsson et al. (2004) found the factory grinding stage to affect solution viscosity only slightly, while laboratory grinding was found not to affect viscosity at all. The most probable sources affecting molecular weight distribution (MWD) may be due to variations in raw materials and materials introduced in production process, such as in dissolution. It was investigated by Stigsson et al. (2004) that production steps are unlikely to have a significant effect on MWD. The same results were effectively concluded for evenness of substitution as well. Only a relatively high temperature in mercerization step hindered the even distribution of substituents. Interestingly, high temperature in the etherification step did not seem to noticeably effect the evenness of substitution. It should be noted however, that reliable standards for determining MWD and evenness of substitution are lacking.

Section 2.1 also pointed out that there is a direct relation between the degree of substitution and solution viscosity. The degree of substitution is also a significant controllable variable in the production of CMC, so the investigation of DS in the process steps as a controllable variable is its own subject and is examined in Section 4.2.3.

Finally, there are many reliable methods for determining the viscosity attribute – or rheological requirements – of the final product. Stigsson et al. (2004) names two useful analysis methods for determining viscosity: Brookfield viscometer and Haake rheometer. Brookfield viscometer gives fast results with low operation costs, but strain rate dependence and thixotropic behavior are out of its range. Haake rheometer can be used then as a complementary method for measuring strain rate dependence and thixotropic behavior, but it is not robust enough for routine use. Both analyses require manual sampling and laboratory analysis. Hence, the lack of automatic (online) measurement hinders the implementation of automated viscosity control in CMC production.

4.2.2 Purity

As was previously stated in Section 3.6, purification happens mainly in the washing stage, using a water-alcohol mixture. Salts, which are by-products of etherification, are removed in the washing process. Therefore, besides washing, an essential way to control the purity variable then is to control reaction kinetics in the etherification process. The temperature range of etherification is around 50–70 ºC (Ambjörnsson et al., 2013). The reaction temperature is raised after mercerization, as it is known to

minimize salt production in etherification (Stigsson et al., 2004). The optimal temperature must be settled case by case, mainly due to variation caused by different raw materials. Besides temperature, Yeasmin & Mondal (2015) noted that a higher NaOH concentration drives sodium glycolate formation in etherification. In their production case of synthesizing CMC from corn husks, they noted that while NaOH concentration contributes directly to a higher degree of substitution, it also reacts with MCA, contributing to the formation of salt, sodium glycolate (Equation 3), while also inactivating the MCA. They concluded from other studies as well, that passing the optimum concentrations for NaOH and MCA starts favoring the unwanted side reaction, instead of the degree of substitution.

Besides testing the produced CMC samples, no quicker methods exist for testing results of etherification. The samples are usually tested for different impurities with different methods after milling stage and after CMC is completely dried. For example, NaCl content can be clarified through a titration of a sample, so implementing an online feedback may be complicated.

4.2.3 Degree of substitution

Degree of substitution is the final controllable variable to be investigated, yet it is perhaps the most important. DS has been studied previously in Sections 2.1.3 and 2.3.4, where it was concluded, that DS defines some of the most essential physical and chemical functional properties of CMC. As such, improving the DS value in cellulose derivatives is a rich and active topic in the field of cellulose chemistry.

Degree of substitution is determined mainly by reaction kinetics – more precisely etherification conditions. This includes common factors in reactor conditions, but also different cellulose sources, optimal solvent ratios and amounts, and volumes of both solvents and raw materials have been found to affect the DS (Yeasmin & Mondal, 2015). There is a lot of room for variation in process control concerning the DS, but universal process conditions do not exist. Meeting the correct conditions and reaching a high degree of substitution is a problem that must be solved case by case.

It is known that concerning reactor conditions, temperature and reaction time carry a significant role in optimizing the DS (Yeasmin & Mondal, 2015). For example, Saputra

et al. (2014) used 60 ºC for CMC synthesis from water hyacinth, and produced CMC with the substitution of 1.67. However, their reaction time was unspecified. Yeasmin & Mondal (2015) found 55 ºC to be the optimal etherification temperature for CMC from corn husks, with a very high DS of 2.42. They showed with 6 different samples that the DS rises steadily in the reactor for 3.5 hours. However, Stigsson et al. (2004) concluded that minor deviations from the reactor temperature program bears little effects on the overall quality of the product.

Besides reactor temperature and time, cellulose particle size, and reaction kinetics like chemical concentrations (NaOH and MCA) have also shown to be affecting the substitution process (Yeasmin & Mondal, 2015). The reactions have been reviewed more closely in Section 2.3. Yeasmin & Mondal (2015) found optimal NaOH concentration for substitution to be around 30 % weight per volume, while Saputra et al. (2014) found 10 % of aqueous NaOH to yield the highest DS value. MCA must be added into the reactor in proportion to NaOH to reach the optimal DS value; Yeasmin & Mondal (2015) discovered around 12.7 moles per liter of MCA to reach the highest DS. Finally, cellulose particle size was found to affect the DS inversely; the smaller particles yield higher DS. This is likely because of the increased total reactive surface area of the smaller particles. It can be assumed that the particle size is well controlled in industrial CMC production as sieves are used to classify the ground cellulose.

Being a powder-like substance, the determination of DS is possible by numerous means. Yeasmin & Mondal (2015) lists many techniques and methods for the determination of the DS: chemical methods, ASTM D1439, Raman spectroscopy, and IR Sem-EDX. The methods can be divided into classical and modern methods. The classical determination methods are chemical titrimetric determination methods, based on the exceptional acidity of carboxylic acid, with the most common method being the back-titration method (Şahin, 2018), where the sodium salt is converted into acid and mixed with NaOH. The DS value is then calculated by the remaining quantity of NaOH. Chemical measuring methods can be problematic, as they can be time-consuming and may include handling of hazardous chemicals.

Sahin (2018) mentions modern methods, such as spectroscopic and chromatographic methods. Modern methods tend to rely on expensive equipment, but on the other hand,

can consider sources of error such as stoichiometric interactions at higher DS values, and do not require highly experienced personnel.

NIR (near-infrared) and Raman are modern and complementary spectroscopic methods used in DS determination, based respectively on light absorption and light scattering. Stigsson et al. (2004) showed that NIR enables online measurement of CMC samples, having a strong impact to real-time quality control.

4.3 Summary of process control

Finally, Table 1 are lists and summarizes significant manipulated and controllable variables discussed in this work. It should be noted that the washing process consists of two sub-processes (Tiihonen, 2017): the washing tank performs the thickening of the liquid, while the flat filter handles the purifying. In this table, no single drying method is inspected, but the variables are mainly generalizations.

Table 1. Significant variables within process steps.

Process step	Manipulated variable(s)	Controlled variable(s)
Cellulose grinding	Time	Particle size
Mercerization,	Temperature, time, concentrations	Swelling, yield
Etherification	Temperature, time, concentrations	Degree of subst., evenness of subst., yield
Neutralization	HCl amount	pH
Washing	Solvent amount, solvent flow rate	Liquid thickening, purity; salt content
Drying	Temperature, drying air moisture and flow rate, time	Moisture
Granulation	Steam feed, residence time, stirring speed	Particle size, density

5 SUMMARY

The aim of this bachelor's thesis was to build a process description of CMC production.

Section 2 of this work was an assessment describing basic process knowledge concerning CMC production, divided into three topics: product quality attributes, raw materials, and chemistry. The first subsection was an investigation of product quality attributes, of which solution viscosity, purity, and the degree of substitution were deemed to be the most significant ones. It was found that none of the product quality attributes are binary by nature, but generally exhibit certain ranges that can be useful to particular grades of CMC. In the second subsection, common raw materials were listed. A couple of potential and unorthodox sources of cellulose were explored, pointing out the vast range of possible raw materials. Finally, the third subsection investigated the chemical phenomena behind cellulose and CMC synthesis. It was concluded that the dissolution of cellulose is a problematic task due to cellulose's chemically resilient nature, and has led to the development of a wide variety of possible solvents and solvent mixtures. It was also concluded that the two main reactions of CMC synthesis are mercerization and etherification. Etherification was found to be the central factor in determining the product quality attributes.

In Section 3, the industrial production process of CMC was inspected, using as an example the production line from Nouryon in Äänekoski. It was shown that the industrial production line consists of eleven subprocesses, where purified grades are also processed through a washing unit, unlike technical grades. Descriptions of all the subprocesses were given.

Section 4 of the work concentrated on process control in CMC production. Process control was inspected through manipulated variables and controllable variables. The most probable factors causing variation in CMC production were found to be raw cellulose variations, differences in reactor operations, and later process steps, mainly storage vessels, washing and drying processes. The main manipulated variable in the reactor was found to be temperature, which was used to control cellulose swelling, yield, degree of substitution, degree of evenness, and salt production. It was also hypothesized, that

product variance could come from an uneven flow dampening in buffer tank, and from incomplete washing and drying operations.

The main controllable variables in Section 4 were found to be the same features as product quality attributes: solution viscosity, purity, and the degree of substitution. It was concluded that they are affected by many different factors and process steps. Solution viscosity was found to be directly proportional to the length of the polymer chains, molecular weight distribution, evenness of substitution, and the degree of substitution. Also, the etherification step was found to be the main process step to control solution viscosity. Brooke viscometer and Haake rheometer were found to be useful, complementary analysis methods for analyzing solution viscosity. The purity variable was shown to be the controlling of salt content in the product, where deviation from optimal NaOH and MCA concentrations favored salt production. Of the process step, washing and etherification were determined to be the main steps in controlling purity. Titration was concluded to be a common way in analyzing purity. Finally, many factors were found to be affecting the degree of substitution. The DS was found to be controlled by common factors in reactor conditions (temperature and time), but also different cellulose sources (cellulose particle size), and optimal ratios and concentrations of raw materials (NaOH and MCA). Again, the etherification step was shown to be the main process step in controlling the DS, hence making it the central process step in controlling quality attributes. Many methods for analyzing the DS were listed, some with the possibility of online measurement. It was finally concluded that universal process conditions for CMC production do not exist.

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